*Polyhedron* Vol. 8, No. 2, pp. 211–214, 1989
Printed in Great Britain

0277–5387/89 \$3.00+.00

# ADDUCTS OF COORDINATION COMPOUNDS—XIV.* THE NATURE OF POULENC'S SILVER BROMIDE, "$[Rh(py)_4Br_2Ag]Br_2$"

R. D. GILLARD,† SIMON H. MITCHELL and DYFRIG J. THOMAS

Department of Chemistry, University of Wales, P.O. Box 912, Cardiff CF1 3TB, Wales, U.K.

(*Received* 29 *July* 1988; *accepted* 25 *August* 1988)

**Abstract**—The 1 : 1 adducts of silver bromide with the complex salts *trans*-$[M(py)_4X_2]Br$ (py = pyridine; M = Rh, X = Br—Poulenc's compound; M = Rh or Ir, X = Cl—newly synthesized compounds) are salts, *trans*-$[M(py)_4X_2](AgBr_2)$, of the dibromo-argentate(I) ion ($\nu_3$ at *ca* 240 $cm^{-1}$), rare in solid species.

Large cations like tetraphenylarsonium and phosphonium ($Ph_4E^+$; $Ph = C_6H_5$; E = P or As) containing flat aromatic substituents on a central atom are commonly used to precipitate anions. Pyridine based cations often precipitate unusual anions. For example, [diquat] bromide treated with bromine yields[2] $[diquat](Br_3)_2$ and the paraquat salt of the $InI_5^{2-}$ ion is stable.[3] In a similar way, cations *trans*-$[RhL_4X_2]^+$ (L = an N-heterocycle like pyridine, X = chloride or bromide) form salts with common anions (like halide or nitrate) which themselves readily give rise to adducts with a surprising range of substances. Many of the adducts have interesting or unusual components.

Among those which have been studied are several (chiefly of the dibromo–pyridine cation above, abbreviated to B here) initially discovered[4] by Poulenc. These include: $[B](NO_3)HNO_3$, a hydrogen dinitrate; $[B](NO_3)AgNO_3$, a dinitratoargentate(I)—these two types form the subject of the previous paper[1] in this series; $[B](H_5O_2)Br_2$,[5] and [B]BrAgBr, formulated by Poulenc as *trans*-$[Rh(py)_4Br(BrAg)]Br_2$, a possible structure again supported recently.[6] Our present note reformulates the last as the dibromoargentate(I), only the second example of such a solid salt. We have also made the analogous chlororhodium and chloroiridium(III) compounds, by precipitation. For completeness, the many other adducts, solvates and the like, including salts of trihalide ions, may be mentioned.

The interactions via chloride or bromide ions, of silver(I) with rhodium(III) or iridium(III) are of particular interest, because of the much-used but ill-understood "rhodium effect" and "iridium effect" on the speed of photographic emulsions (usually achieved technically[7] by adding simple or complex halides of these platinum metals to the precipitating emulsion of silver halide).

## RESULTS AND DISCUSSION

Poulenc obtained[4] his adduct *trans*-$[Rh(py)_4Br_2](AgBr_2)$ in rather low yield while trying to remove bromide coordinated to rhodium(III) by precipitation. We find that the same product may be obtained in high yield by a much simpler scheme (1):

$$trans\text{-}[Rh(py)_4Br_2]Br + (AgBr_2)^- \longrightarrow trans\text{-}[Rh(py)_4Br_2](AgBr_2). \quad (1)$$

This reaction of *trans*-$[Rh(py)_4Br_2]Br \cdot 6H_2O$ with AgBr dissolved in saturated aqueous potassium bromide by either of the two methods was successful.

(1) An aqueous or 25% (v/v) aqueous ethanol solution of the complex was added to and rapidly mixed with the aqueous KBr–AgBr solution. *Trans*-$[Rh(py)_4Br_2]AgBr_2$ immediately precipitates as an orange–yellow powder.

(2) *Trans*-$[Rh(py)_4Br_2]Br$ ground with the aqueous KBr–AgBr solution changes rapidly to a fine powder of the product.

The analogous (and isomorphous) salts of iridium(III) and of dichlororhodium(III) were made by the first method. All three compounds decompose

---

* For part XIII, see ref. 1.

† Author to whom correspondence should be addressed.

in water because of the insolubility of silver bromide.

$$[M(py)_4X_2](AgBr_2) \longrightarrow AgBr\downarrow + [M(py)_4X_2]^+_{(aq.)} + Br^-_{(aq.)}.$$

The IR spectrum of *trans*-$[Rh(py)_4Br_2](AgBr_2)$ is very similar to that of its parent *trans*-$[Rh(py)_4Br_2]Br\cdot 6H_2O$. There is one new band at 240 $cm^{-1}$. This probably arises from the Ag—$Br_2$ asymmetric stretch $\nu_3(\Sigma_u^+)$. There is a general paucity of data[6,8] on Ag—Br modes. The careful study[8b] of $[N(CH_3)_4][AgX_2]$ dissolved in tri(*n*-butyl)phosphine oxide by Waters and Basak placed the IR active $\nu_3(\Sigma_u^+)$ mode of $AgBr_2^-$ at 253 $cm^{-1}$. Bottger and Geddes[8c] isolated solid salts of the stoichiometry $[E(CH_3)_4](AgBr_2)$ (E = N or P), but their vibrational spectra strongly suggested that the anions were made up by linked $AgX_4$ tetrahedra, and certainly did not contain linear two-coordinate silver ions.

IR spectra are recorded in Table 1.

Similarly, for the new iridium compound, *trans*-$[Ir(py)_4Cl_2](AgBr_2)$, the spectra confirm the presence of pyridine (1650, 776, 709 $cm^{-1}$) and the presence of a pyridine–Ir bond (339 $cm^{-1}$). The only notable difference between the parent and adduct is again the absorption (which we assign as $\nu_3$) at 238 $cm^{-1}$ of the adduct.

The solubility of silver halides in aqueous silver salts and aqueous halides is well known and understood. The relevant stability constants[6,11] indicate that the chief species in excess of *aqueous* halide $X^-$ are $AgX_2^-$ (while compounds like $(NH_4)_2AgBr_3$ may be made, for example in methylethyl ketone, they are insensitive to light). A simple method[12] of making large crystals of silver chloride depends on the slow reversal of (2).

$$HCl + AgCl \rightleftharpoons \text{"}H[AgCl_2]\text{"}. \qquad (2)$$

So the anion $AgX_2^-$ (X = halide) has long been recognized[13] as a solution species, but in the solid state there are few examples.[14] Poulenc's compound has been proposed[15] as a further example, without structural work. It is the last of those remarkable adducts which were originally reported[4] by Poulenc to be dealt with in this series (cf. *trans*-$[Rh(py)_4Br_2](H_5O_2)Br_2$,[5] *trans*-$[Rh(py)_4Br_2][H(ONO_2)_2]$[1,16] and *trans*-$[Rh(py)_4Br_2][Ag(ONO_2)_2])$.[1]

In the first established example[14] of a linear silver dibromide anion, $[Au(dtc)_2]AgBr_2$, the silver atom is linearly coordinated by bromine and lies on a special position in the lattice. There is[17] an analogous but not isomorphous gold compound, containing linear $AuBr_2^-$.

Besides $AgBr_2^-$, there are a small number of monomeric linear cationic $AgX_2^+$ or anionic $AgX_2^-$ complexes (X = $NH_3$,[18,19] py[20] and NCO[21]), so this structure for $AgBr_2^-$ is not too unexpected. However it is much rarer than would be thought in view of its common occurrence in solution.

Instead of the two coordinated linear dihaloargentate(I) structures expected from solution studies, distorted tetrahedral coordination of silver by hal-

Table 1. Selected IR bands (in $cm^{-1}$) of *trans*-$[M(py)_4X_2]Y$

| Mode | M = Rh, X = Br, Y = $AgBr_2$ | M = Ir, X = Cl,[a] Y = $Cl\cdot 6H_2O$ | M = Ir, X = Cl,[b] Y = $AgBr_2$ |
|---|---|---|---|
| py | — | 1650 | 1650 |
| py | — | 776 | 776 |
| py | — | 709 | 709 |
| py($\nu_{27}$) | $466_w$ | — | — |
| $Rh_{py}$ | $340_w$ | — | — |
| $Rh_{py}$ | $311_w$ | — | — |
| IrCl | — | 338 | 338 |
| Ag—Br[c] | 239m[d] | — | 238 |

[a] For crystal structure see ref. 9.

[b] Our methods produced powders. In view of the aqueous insolubility of the compounds, it may be necessary to employ a different solvent system to prepare crystals. $AgX_2^-$ is stable[10] in DMSO, which might be suitable.

[c] The chloride analogue *trans*-$[Rh(py)_4Cl_2](AgCl_2)$ could not be prepared by our present methods, so a different solvent system might also be needed.

[d] $\nu_3(\Sigma_u^+)$ of linear $[AgBr_2]^-$.

ide is common in the solid state. The tetrahedra may be paired, sharing edges [$Ag_2I_6^{4-}$],[22] or linked together to form chains, either single $AgX_2^-$ (X = Br or I)[23] and $AgI_3^{2-}$,[24] or double $Ag_2I_3^-$ [25,26] and $Ag_3I_4^-$ [27] (but this last one also has a silver atom occupying an octahedral hole between each pair of double tetrahedra). One other arrangement is found: a polymer of edge-sharing trigonal bipyramids ($AgX_2^-$, X = Cl[28] or Br[29]).

None of the known silver halide–silver nitrate double salts contains a simple linear X—Ag—X sequence. Usually the silver and halide form a polymeric structure, and there are several distinct types of silver atoms. In the few cases where an almost linear sequence *is* found, there is always nitrate also coordinated to the silver.[30–32]

In view of the frequent similarity (diagonal relationship) between $S^{2-}$ and $Br^-$, the existence[33] of the linear ion $AgS_2^{3-}$ containing two coordinated silver (isoelectronic with $AgCl_2^-$) in the salt $Na_3AgS_2$ is interesting. Nevertheless, salts of linear $AgBr_2^-$ are extremely rare, and it is interesting that Poulenc's salt precipitates this monomeric anion.

## EXPERIMENTAL

IR spectra were measured in Nujol mulls, and X-ray photographs used Cu-$K_\alpha$ radiation and 6 h exposure.

### trans-[$Ir(py)_4Cl_2$]$Cl \cdot 6H_2O$

A known synthesis[9] was used, substituting commercial iridium trichloride for $K_3IrCl_6$. $IrCl_3$ (0.507 g) dissolved in water (18 cm$^3$), with pyridine (6.5 cm$^3$) and ethanol (3 cm$^3$) was heated (steam bath) for 20 min. The solution was made acid (conc. HCl) and cooled in ice. The yellow crystals which formed were collected and crystallized from water. Yield 56%. An aqueous solution ($4.52\times10^{-5}$ M) showed peaks at 255.8 and 195.7 nm. The former had a molar extinction coefficient, ε, of 20,974, close to Jørgensen's value[34] (which confirms the presence of 4 mol of pyridine per iridium).

### trans-[$Ir(py)_4Cl_2$]($AgBr_2$)

To 30 cm$^3$ of saturated aqueous KBr, $AgNO_3$ solution was added until the first sign of a permanent precipitation: saturated KBr was added dropwise until the precipitate just disappeared. This was now a saturated KBr/AgBr solution containing silver(I) chiefly as [$AgBr_2$]$^-$ (see text). *trans*-[$Ir(py)_4Cl_2$]Cl (0.256 g) was dissolved in water (30 cm$^3$) by gentle warming. The KBr/AgBr solution was mixed with this solution and left in the dark for 1 h. The precipitate was washed thoroughly with saturated KBr solution, to remove any traces of solid AgBr; it was then washed with water. The precipitate was dried in a desiccator over conc. $H_2SO_4$. Yield = 0.253 g (72%).

The adduct (0.0729 g, $8.61\times10^{-5}$ mol) was boiled in water for 20 min in the dark. The silver bromide formed was collected and washed with water, ethanol and finally ether, then weighed (0.01588 g, $8.41\times10^{-5}$ mol).

### trans-[$Rh(py)_4Cl_2$]($AgBr_2$)

Saturated KBr/AgBr was added to a solution of *trans*-[$Rh(py)_4Cl_2$]Cl (0.3141 g/30 cm$^3$). A yellow precipitate immediately formed. This was collected and washed throughly with saturated KBr solution, then with water. The powder was dried in a desiccator over conc. $H_2SO_4$. Yield = 0.3314 g (73.6%). An X-ray powder diffraction photograph was taken (Cu-$K_\alpha$ radiation for 6 h).

### *Poulenc's compound:* trans-[$Rh(py)_4Br_2$]($AgBr_2$)

Poulenc's original method[4] and the precipitation were used. The products from both reactions were washed with saturated aqueous KBr to remove AgBr, then with water and finally ethanol. The yield by method (2) is 93.8%. Found: C, 28.7; H, 2.3; N, 6.3. Calc. for $C_{20}H_{20}AgBr_4N_4Rh$: C, 28.4; H, 2.4; N, 6.6%.

*Acknowledgements*—We thank Dr B. W. Delf for help with X-ray powder photography.

## REFERENCES

1. R. D. Gillard and S. H. Mitchell, *Polyhedron* 1987, **6**, 1885.
2. (a) R. M. Thomas, F. R. Gerus and J. L. Sands, German patent 1,953,230 (1970); *Chem. Abstr.* 1970, **73**, 14708; (b) Great Lakes Chem. Corp., French patent 2,173,830 (1973); *Chem. Abstr.* 1974, **80**, 108566.
3. G. Contreras and D. G. Tuck, *J. Chem. Soc., Dalton Trans.* 1973, 922.
4. P. Poulenc, *Annls Chim.* 1935, **4**, 567.
5. D. Dollimore, R. D. Gillard and E. D. McKenzie, *J. Chem. Soc.* 1965, 4479.
6. R. J. Lancashire, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 5, pp. 775 and 822–823. Pergamon Press, Oxford (1987).
7. (a) J. M. Harbison and M. E. Spencer, in *The Theory of the Photographic Process* (Edited by T. H. James), 4th edn, pp. 149 and 157. Macmillan, New York (1977); (b) Metal Dopants, abstracts 338–344 in *Papers of the International Congress of Photographic*

*Science* (Edited by H. H. Adam), pp. 176–187. Royal Photographic Society of Great Britain, Cambridge (1982); (c) D. D. Chapman and E. R. Schmittou, in *Comprehensive Coordination Chemistry* (Edited by E. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 6, p. 95. Pergamon Press, Oxford (1987).

8. (a) G. L. Bottger and A. L. Geddes, *Spectrochim. Acta* 1967, **23A**, 1551; (b) D. N. Waters and B. Basak, *J. Chem. Soc. A* 1971, 2733; (c) G. L. Bottger and A. L. Geddes, *Spectrochim. Acta* 1967, **23A**, 1551.
9. R. D. Gillard, S. H. Mitchell, P. A. Williams and R. S. Vagg, *J. Coord. Chem.* 1984, **13**, 325.
10. B. Bry and B. Tremillon, *J. Chem. Res.* (*S*) 1979, 156; B. Bry and B. Tremillon, *J. Chem. Res.* (*M*) 1979, 1884.
11. (a) G. I. P. Levenson, in *The Theory of the Photographic Process* (Edited by T. H. James), 4th edn, p. 437. Macmillan, New York (1977); (b) J. Pouradier, A. Pailliolet and C. R. Berry, in *The Theory of the Photographic Process* (Edited by T. M. James), 4th edn, p. 7. Macmillan, New York (1977).
12. J. C. Bailar, *Inorg. Synth.* 1980, **20**, 18.
13. L. G. Sillen, The Chemical Society, special publication No. 17 (1971); L. G. Sillen, The Chemical Society, special publication No. 25 (1964).
14. J. A. Cras, J. H. Noordik, P. T. Beurskens and A. M. Verhoeven, *J. Cryst. Mol. Struc.* 1971, **1**, 155.
15. A. W. Addison and R. D. Gillard, *J. Chem. Soc., Dalton Trans.* 1973, 2009.
16. (a) R. D. Gillard and R. Ugo, *J. Chem. Soc.* 1966, 549; (b) R. D. Gillard and R. Ugo, *Abstract B4, Chem. Soc. Autumn Meet.* Nottingham (September 1965).
17. P. T. Beurskens, H. J. A. Blaauw, J. A. Cras and J. J. Steggerda, *Inorg. Chem.* 1968, **7**, 805.
18. H. M. Maurer and A. Weiss, *Z. Kristallogr.* 1977, **146**, 227.
19. T. Yamaguchi and O. Lindqvist, *Acta Chem. Scand.* 1983, **A37**, 685.
20. S. Menchetti, G. Rossi and V. Tazzoli, *Rc. Ist. Lomb. Sci. Lett. A.* 1970, **104**, 309.
21. K. Aarlot and K. Ase, *Acta Chem. Scand.* 1974, **A28**, 137.
22. H. J. Keller, B. Keppler and H. Pritzkow, *Acta Cryst.* 1982, **B38**, 1603.
23. R. Stomberg, *Acta Chem. Scand.* 1969, **23**, 3498.
24. C. Brink and C. H. MacGillavry, *Acta Cryst.* 1949, **2**, 158.
25. H.-J. Meyer, *Acta Cryst.* 1963, **16**, 788.
26. C. Brink, N. F. Binnendijk and J. van de Linde, *Acta Cryst.* 1954, **7**, 176.
27. C. J. Gilmore, P. A. Tucker and P. Woodward, *J. Chem. Soc. A* 1971, 1337.
28. H. C. Gaebell, G. Meyer and R. Hoppe, *Z. Anorg. Allg. Chem.* 1983, **497**, 199.
29. H. C. Gaebell and G. Meyer, *Z. Anorg. Allg. Chem.* 1984, **513**, 15.
30. K. Persson, *Acta Cryst.* 1979, **B35**, 1432.
31. K. Persson and B. Holmberg, *Acta Cryst.* 1977, **B33**, 3768.
32. R. Birnstock and D. Britton, *Z. Kristallogr.* 1970, **132**, 87.
33. K. O. Klepp and W. Bronger, *J. Less-common Metals* 1985, **106**, 95.
34. C. K. Jørgensen, *Absorption Spectra and Chemical Bonding.* Academic Press, London (1962).